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The study of the transition state of bimolecular reactions using negative ion photodetachment is described. The I + HI reaction is used as an example of this method. The photoelectron spectrum of IHI^- shows resolved vibrational features assigned to a progression in the antisymmetric stretch mode of the neutral IHI complex. Threshold photodetachment studies of this system at higher resolution show additional structure that arises from two sources: (1) resonances supported by the I + HI potential energy surface and (2) transitions to nearly free internal rotor states of the IHI complex. The photoelectron spectrum of the cluster anion $IDI^-(N_2O)$ is also described.

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Department of Chemistry
University of California
Berkeley, CA 94720

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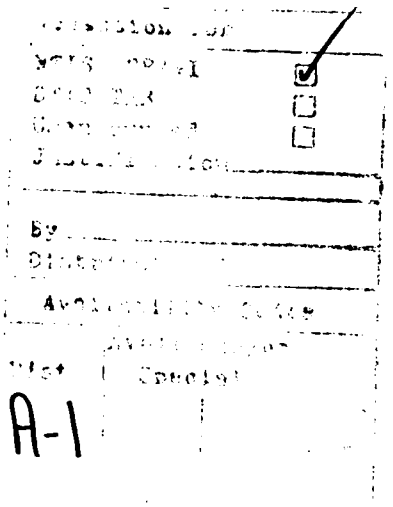

Negative Ion Photodetachment as a Probe of the Transition State Region: The I + HI Reaction

Daniel M. Neumark*
Department of Chemistry
University of California
Berkeley, CA 94720

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* NSF Presidential Young Investigator and Alfred P. Sloan Fellow

INTRODUCTION

Experimental investigations of molecular vibrations can be split into studies of bound and unbound systems. In the case of bound systems, the emphasis in recent years has been on improving spectral resolution in order to better understand the vibrational motion of molecules and clusters. For unbound systems, dynamical as well as spectroscopic issues are of importance. A vital dynamical question is whether the lifetime of the system of interest with respect to, for example, dissociation or electron ejection is sufficiently long so that any resolved vibrational structure can be observed. If this condition is satisfied, then one can use the observed peak positions and linewidths to learn about both the spectroscopy and dynamics of the unbound system. The literature abounds with examples of this in studies of predissociating,[1] autoionizing,[2] and autodetaching[3] systems.

In this chapter, we discuss experiments in our labororatory which probe the vibrational motion associated with an unbound system of paramount importance in chemical physics: the transition state of a chemical reaction. These 'transition state spectroscopy' experiments allow the powerful techniques of spectroscopic analysis to be applied to the study of the potential energy surfaces that govern chemical reactions. Our experiments are based on the idea that the transition state region of the potential energy surface for a neutral bimolecular reaction can be accessed by photodetaching a stable negative ion, so long as the geometry of the negative ion is similar to that of

the neutral transition state. We define the 'transition state region' of a potential energy surface to be the region of the surface where the properties of the complex formed in a reactive collision are distinct from separated reactants or products; this definition broadly covers the region where chemical bond cleavage and formation occurs, and is intended to be more general than the classical definition of the transition state in transition state theory.

a) Background

Before describing our photodetachment experiments in detail, it is instructive to discuss some of the previous and ongoing investigations in the field of transition state spectroscopy. The goal of these studies is to probe the transition state region directly, rather than simply measure product distributions as is typically done in state-to-state scattering experiments. Transition state spectroscopy can be divided into 'full collision' experiments, in which one attempts to study the short-lived complex formed in a reactive collision, and 'half-collision' experiments in which a repulsive or reactive potential energy surface is probed via photoexcitation of a bound species. In principle, 'full collision' experiments are more general because reactive collisions, by definition, must sample the transition state region of the potential energy surface. In 'half collision' experiments, one must be certain that the initial bound species has good geometric overlap with the

transition state region of the surface accessed via photoexcitation. However, 'half collision' experiments often allow one to probe the transition state region under better-defined initial conditions than 'full collision' experiments.

The first transition state spectroscopy experiments were the full collision studies of Polanyi,[4] Brooks,[5] and their co-workers in 1980. Polanyi reported the observation of chemiluminescence from the F-Na-Na complex formed in the F + Na_2 reaction. In Brooks's experiments, which have focussed on the reaction K + NaCl $\rightarrow$ Na + KCl,[6] the [KNaCl] complex formed in the is electronically excited with a tunable laser, and the Na* which results from decomposition of the [KNaCl]* complex is monitored by emission. Experiments of this type have also been performed by Kompa[7] and Burnham,[8] in which laser excitation of the [$XeCl_2$] complex formed in a Xe + Cl_2 collision yields emission from XeCl*, and by Kleiber et al.[9] on the Mg + H_2 reaction. Morgner has used Penning ionization to probe the complex formed in collisions of metastable He with halogen molecules.[10] The most intriguing 'full collision' transition state spectroscopy experiments have been performed by Valentini and co-workers.[11] Their state-resolved measurements on the H + H_2 and D + H_2 reactions show evidence for reactive resonances associated with quasi-bound states of the [H_3] complex. These experiments, which are described in detail elsewhere in this volume, are the only 'full collision' studies which show any hint of vibrational structure associated with the transition state.

With the exception of Valentini's experiment, the full collision experiments described above require laser excitation of an extremely short-lived collision complex ($<10^{-13}$ sec) under the poorly-defined initial conditions typical of a scattering experiment: neither reactant orientation nor total angular momentum is well-defined. Thus, in addition to the experimental difficulties involved in observing such a short-lived species, the electronic spectroscopy of these species is expected to be complex and difficult to interpret.

These problems are mitigated to some extent in 'half collision' studies. In one class of these experiments, photoexcitation of a stable van der Waals molecule is used to initiate a reaction on either a ground or excited state potential energy surface. Wittig and co-workers[12] studied the reaction H + $CO_2 \rightarrow$ OH + CO via photodissociation at 193 nm of the HBr entity in the van der Waals molecule $CO_2 \cdot HBr$; this restricts the range of reactant orientations contributing to reaction and the resulting OH product state distribution differs from the conventional bimolecular reaction of the same translational energy. Breckenridge et al.[13] have used excitation of the $Hg \cdot H_2$ van der Waals molecule to access the potential energy surface for the excited state reaction $Hg(^3P_1) + H_2 \rightarrow HgH + H$. By monitoring the HgH product yield as a function of the laser frequency used to excite the $Hg \cdot H_2$ complex, they obtain structured 'action spectra' characteristic of the $[HgH_2]^*$ complex on the reactive potential energy surface. In another important set of 'half

collision' experiments, performed by Imre et al.,[14] Kleinermanns,[15] and Butler,[16] a stable molecule is excited to a repulsive electronic potential energy surface and the dispersed fluorescence from the dissociating fragments is observed. The vibrational progressions in the dispersed fluorescence spectra are sensitive to the dynamics on the excited state surface.

The above experiments are examples of frequency-resolved 'half-collision' studies. Zewail and co-workers[17],[18] have pioneered the development of time-resolved 'half-collision' experiments in which femtosecond laser pulses are used to monitor the progress of a chemical reaction in real time. For example, they have performed pump and probe experiments on the $CO_2 \cdot HI$ complex[17] in which the first laser pulse initiates reaction within the complex via photodissociation of the HBr, and the second pulse monitors the appearance of the OH product as a function of time. This provides a 'real-time clock' of the H + CO_2 reaction. Real time pump and probe experiments have also been used to study the photodissociation of ICN and HgI_2.[18] In these experiments, the photofragments are monitored in the transition state region as well as the asymptotic region of the potential energy surfaces on which dissociation occurs. By determining how the spectroscopy of the nascent photofragments evolves as the reaction proceeds, one can, in principle, obtain a very detailed description of the dissociation process.

b) Photodetachment probes of the transition state

We have developed a 'half-collision' experiment which draws on several of the ideas developed in the experiments described above. Our experiment also draws on earlier work by Lineberger[19] and Brauman,[20] in which photodetachment of a stable anion results in a neutral species unstable with respect toeither isomerization or dissociation. In our experiments, a stable negative ion serves as the precursor to the transition state of a neutral bimolecular reaction. This method is most suitable for the study of hydrogen transfer reactions $A + HB \rightarrow HA + B$, where A and B can be atomic or polyatomic species. We can then probe the unstable [AHB] complex formed in the reaction by photodetaching the stable, hydrogen-bonded negative ion AHB^-.[21] If the ion geometry is similar to that of the neutral transition state, then photodetaching the ion will probe the transition state region of the A + HB potential energy surface. Even though the [AHB] complex is unstable, the photoelectron spectrum of AHB^- can exhibit resolved vibrational structure which yields considerable insight into the spectroscopy and dissociation dynamics of the [AHB] complex. Hydrogen transfer reactions are particularly appealing because, in many cases, the transition state region for the reaction has good geometric overlap with the strongly hydrogen-bonded ion AHB^-. In addition, most hydrogen transfer reactions are 'Heavy + Light-Heavy' reactions, in which a hydrogen atom is transferred between two much heavier species. The dissociation dynamics of the [AHB] complex with this mass

combination favors the observation of resolved vibrational structure in the AHB^- photoelectron spectrum. In essence, we observe the fast vibrational motion of the light H atom as the complex slowly dissociates.

This experiment provides a high degree of control over important parameters of a chemical reaction. Photodetachment initiates the A + HB reaction with the atoms in the same geometry as they are in the ion AHB^-, thereby providing excellent control over the reactant orientation. In addition, since the ions are generated in a source which produces rotationally cold species, we can limit the total angular momentum available to the reaction. The latter restriction is particularly significant since it facilitates comparison with theoretical simulations of our results.

The simplest reactions amenable to this method are those in which a hydrogen atom is exchanged between two like or unlike halogen atoms. We have presented results on the symmetric reactions Cl + HCl,[22] I + HI,[23] and Br + HBr[24] which were studied via photoelectron spectroscopy of $ClHCl^-$, $BrHBr^-$, and IHI^-. The photoelectron spectra of these ions show resolved vibrational progressions assigned on the basis of isotope shifts to the ν_3 antisymmetric stretch vibration of the unstable [XHX] complex. This vibration involves H atom motion between two essentially stationary halogen atoms and is poorly coupled to the dissociation coordinate of the complex. The spectra show large 'red shifts' in the ν_3 mode relative to diatomic HX, indicating

that photodetachment indeed accesses the transition state region on the X + HX potential energy surface where the H atom is interacting strongly with both X atoms. Simulations of these photoelectron spectra on model X + HX potential energy surfaces[23,24,25,26,27] show that they are quite sensitive to the nature of the transition state region.

In a similar vein, the photoelectron spectra of asymmetric XHY^- bihalide anions allows us to probe asymmetric exchange reactions including Br + HI → HBr + I, Cl + HI → HCl + I, and F + HI → HF + I.[28,29] These spectra also show progressions in the ν_3 mode of the [XHY] complex, although they provide more information on the I + HX product valley of the neutral potential energy surface than on the region near the entrance channel barrier. Finally, we have studied hydrogen transfer reactions such as F + CH_3OH → HF + CH_3O which involve polyatomic reactants.[30] The photoelectron spectrum of CH_3OHF^- again shows vibrational structure assigned to H atom motion between the O and F atoms in the [CH_3OHF] complex.

One feature common to all the photoelectron spectra mentioned above is that the widths of the observed transitions is broader than the experimental resolution. An important question concerning the dissociation dynamics of the neutral complex is the following. Are the peak widths determined solely by the 'lifetime' of the neutral complex, or is there underlying structure which is unresolved in the photoelectron spectra? This question is particularly intriguing with reference to the $BrHBr^-$

and IHI^- spectra which show widely varying peak widths. In order to answer this, we have recently constructed a threshold photodetachment spectrometer[31] with considerably higher resolution than the instrument on which the photoelectron spectra were obtained. The principles behind the two types of measurements are discussed in the following section.

This article focuses on the reaction that has been most amenable to study via negative ion photodetachment: the I + HI reaction. We review our previously published photoelectron spectroscopy work[23] on IHI^- and compare it to new higher resolution results.[32] The newer results indeed reveal fine structure in the [IHI] complex that was obscured at lower resolution. This structure provides definitive evidence for the existence of dynamical resonances in the I + HI reaction. We conclude by presenting results on the photoelectron spectroscopy of the cluster ion $IDI^-(N_2O)$,[29] which represents the first step in determining how a bihalide ion photoelectron spectrum evolves upon the addition of solvating species.

EXPERIMENTAL

The spectra shown below were obtained with two negative ion photodetachment methods: 'fixed-frequency' photoelectron spectroscopy[33] and threshold photodetachment spectroscopy. The instruments used in these studies have been described in detail previously.[24,31,34] In this section we wish only to describe the

principles behind each experiment.

In both experiments, negative ions are generated by expanding a mixture of neutral gases (10% HI in Ar for the results shown here) through a pulsed molecular beam valve, and by crossing the molecular beam with a 1 keV electron beam just outside the valve orifice.[35] This results in the formation of ions in the continuum flow region of the supersonic expansion and the ions should cool internally as the expansion progresses. Negative ions are extracted from the beam, accelerated to 1 keV and mass-selected using time-of-flight mass spectroscopy.[36,37] In our photoelectron spectrometer, the mass-selected ions are photodetached with a pulsed, fixed-frequency laser. The results shown below were obtained with the fourth harmonic of a Nd:YAG laser at a photon energy of 4.66 eV (λ = 266 nm). We then determine the electron kinetic energy distribution of a small fraction of the ejected photoelectrons by time-of-flight. For a single photodetachment event, the electron kinetic energy (eKE) is given by

$$eKE = h\nu - E^-_b - E^0_{int} + E^-_{int} . \qquad (1)$$

Here $h\nu$ is the photon energy and E^-_b is the binding energy of the electron to the anion. This is 3.80 eV for IHI^-, which is the energy required to remove an electron from the ground state of IHI^- to form I + HI(v=0). E^-_{int} and E^0_{int} are the internal energies of the anion and neutral, respectively. Thus, the electron kinetic energy distribution exhibits peaks resulting from transitions between ion and neutral energy levels. In nearly all

cases, the energy resolution of photoelectron spectroscopy is insufficient to discern rotational structure and one only learns about vibrational energy levels of the neutral and (occasionally) the anion. In our spectrometer, for example, the resolution is 8 meV at eKE = 0.65 eV and degrades at higher electron kinetic energies as $(eKE)^{3/2}$.

Considerably higher energy resolution can be achieved with threshold photodetachment spectroscopy. In this experiment, the ions are photodetached with a tunable pulsed dye laser. At a given laser wavelength, only electrons produced with nearly zero-kinetic energy are detected. The zero-kinetic energy spectrum plotted as a function of laser wavelength consists of a series of peaks, each corresponding to an ion→neutral transition. The width of the peaks is determined by the ability of the instrument to discriminate against photoelectrons produced with high kinetic energy. By adapting the methods developed by Müller-Dethlefs et al. for threshold photoionization of neutrals,[38] we have achieved a resolution of 3 cm^{-1} (0.37 meV) with this instrument and were able to obtain a spectrum of SH^- in which transitions between individual rotational levels of the anion and neutral were resolved.[31] In the experiments performed on IHI^-, tunable laser light in the range of 300 nm was required. This was obtained by frequency doubling the output of an excimer pumped dye laser running at 50 Hz. Three laser dyes, rhodamine 590, 610, and 640, were required to cover the frequency range of interest. Frequency doubling was done with a KDP or BBO crystal,

resulting in pulse energies of 3-5 mJ. The operating conditions used in the IHI^- studies resulted in an energy resolution of 1-2 meV.

RESULTS AND DISCUSSION

a) IHI^- Photoelectron Spectrum

The photoelectron spectrum of IHI^- is shown in Figure 1. The spectrum shows three peaks, all of which lie at electron kinetic energies below $h\nu - E^-_b = 0.86$ eV, the kinetic energy that would result if I + HI(v=0) were formed. This value is derived from the laser photon energy (4.66 eV), the electron affnity of iodine (3.0591 eV[39]), and the enthalpy of dissociation of IHI^- into I^- + HI(v=0) (0.74 ± 0.13 eV[40]). Thus, all the peaks correspond to states of the [IHI] complex with sufficient energy to dissociate to I + HI(v=0). In the photoelectron spectrum of IDI^- (Figure 2), three peaks are also observed. The peak at highest electron kinetic energy does not shift, but the spacing between the peaks is less. On this basis, the peaks are assigned to a progression in the ν_3 antisymmetric stretch vibration of the neutral [IHI] complex originating from the $\nu_3" = 0$ level of IHI^-. Since this is not a totally symmetric vibration, only transitions to even ν_3' levels of [IHI] are allowed. The peaks are therefore due to transitions to the $\nu_3' = 0$, 2, and 4 antisymmetric stretch levels of [IHI]. The spectrum shows that the $\nu_3' = 0$ and $\nu_3' = 2$ levels of the complex are separated by 0.174 eV, which is considerably smaller than the HI

vibrational frequency (0.286 eV[41]). Hence we are probing a region of the potential energy surface where the H atom is vibrating in a much flatter potential than in diatomic HI; this is a signature of the transition state region where the H atom interacts strongly with both I atoms.

An interesting feature in the IHI^- and IDI^- photoelectron spectra is the wide variation in the observed peak widths. The widths (FWHM) of the $v_3' = 0$, 2, and 4 peaks in the IHI^- spectrum are 74 meV, 23 meV, and ~50 meV, respectively, while the widths of the corresponding peaks in the IDI^- spectrum are 50 meV, 42 meV, and 13 meV. While one might be tempted to attribute the peak widths to lifetime broadening of the various v_3' levels of the neutral complex, this is a dangerous assumption. The peak widths do not appear to depend in an intuitively simple way on the internal energy of the complex. For example, of the three peaks in the IDI^- spectrum, the narrowest (the $v_3' = 4$ peak) results from the state of the [IDI] complex with the most internal energy. The pattern of the peak widths suggests the possibility that at least some of the peaks are envelopes of transitions which are not resolved in the photoelectron spectrum.

To gain further insight into the IHI^- and IDI^- photoelectron spectra, the spectra have been simulated at various levels of approximation by three different groups.[23,25,26,27] The simulations consist of calculating the Franck-Condon overlap as a function of energy between the ion and the scattering wavefunctions supported by a model I + HI potential energy surface. All three

simulations use the same I + HI surface,[42] a LEPS (London-Eyring-Polanyi-Sato[43]) surface with a collinear minimum energy path and a 1.1 kcal/mol barrier at the saddle point. The same IHI^- geometry and vibrational frequencies are also used. The ion is assumed to be linear and centrosymmetric[44] with an equilibrium interiodine distance of 3.88 Å, and the vibrational frequencies are taken from matrix isolation spectroscopy.[21] In the simulations performed by our group,[23] the bending motion of the ion and complex was neglected and only the symmetric (v_1) and antisymmetric (v_3) stretch vibrations are connsidered. This was considered a reasonable approximation because the combination of a linear ion and a neutral surface which favors the collinear [IHI] geometry leads one to expect little or no bending excitation in the photoelectron spectrum. Gazdy and Bowman[27] have performed three-dimensional simulations of the spectra which include the bending motion and use an L^2 basis for the scattering wavefuunctions. Schatz[25] has simulated the spectra using the exact three-dimensional wavefunctions supported by the I + HI surface. All the simulations assume the ion is in its ground vibrational state and that the total angular momentum J = 0 for the ion and neutral complex.

In all the simulations, the $v_3' = 2$ and 4 features in the IHI^- and IDI^- spectra appear not as single broad peaks, but rather as progressions of peaks spaced by about 12 meV (100 cm^{-1}). The closely spaced peaks represent transitions to metastable symmetric stretch levels of the complex. For example,

the simulation by Schatz, which is the most realistic, shows three closely spaced peaks associated with the $v_3 = 2$ level of [IHI] resulting from transitions to the $v_1 = 0$, 1, and 2 symmetric stretch levels of the complex. The linewidths of these peaks are 2-5 meV, indicating lifetimes of several hundred femtoseconds for these metastable states. These relatively long-lived states are responsible for the sharp resonance structure predicted in quantum mechanical reactive scattering calculations on Heavy + Light-Heavy reactions,[45,46,47] of which I + HI is an extreme example. On the other hand, the transition to the $v_3 = 0$ level of [IHI] (and [IDI]) is predicted to be dominated by overlap with direct scattering wavefunctions; the $v_3' = 0$ level of the complex formed by photodetachment dissociates rapidly. Nonetheless, even the simulated $v_3' = 0$ feature in Schatz's simulation consists of a series of peaks rather than a single broad peak. In summary, a comparison of the experimental and simulated photoelectron spectra strongly suggests that the peaks in the experimental spectra are envelopes for unresolved underlying structure which, if observable, would provide yet another level of insight into the transition state region of the I + HI reaction. The possibility of observing this underlying structure motivated the higher resolution experiments discussed in the next section.

b) Threshold Photodetachment Spectroscopy of IHI^-

The threshold photodetachment spectra of the three peaks in

Figure 1 are shown in Figures 3-5. The horizontal axis at the bottom of each plot shows the photodetachment wavelength λ. For convenient comparison with Figure 1, the top axis shows the corresponding electron kinetic energy (eKE) that would result in a photoelectron spectrum at 266 nm; the two axes are related by $eKE = 1240(1/266 - 1/\lambda)$.

The threshold photodetachment spectrum of the $v_3' = 2$ peak (Figure 3) reveals three partially resolved peaks spaced by approximately 12 meV. The peak widths are about 12 meV, and the intensity of the peaks decreases towards lower wavelength. The observed peak spacing is in the range expected for a progression in symmetric stretch levels of the [IHI] complex. In fact, the experimental peak spacings and intensities are quite similar to the simulations of the $v_3' = 2$ feature. The major difference is that in the simulation by Schatz,[25] the peaks in the symmetric stretch progression are narrower (2 meV) and are therefore fully resolved. Nonetheless, the correspondence between the experimental and simulated spectra strongly suggests we are seeing a progression in quasi-bound [IHI] symmetric stretch states.

Figure 4 shows the threshold photodetachment spectrum of the $v_3'=4$ feature in the IHI^- photoelectron spectrum. Four well-resolved peaks are evident in this spectrum. Peaks A, a, and b are evenly spaced by an interval of 16.0 meV (129 cm^{-1}), while peaks A and B are separated by 12.5 meV (101 cm^{-1}). The peaks are substantially narrower than those in Figure 3; peaks A

and a are 3.7 meV wide, and peak B is 5.6 meV wide.

The presence of two intervals among the peaks in Figure 4 suggests the presence of two progressions. We find that the intensities of peaks a and b are sensitive to the ion source operating conditions. For example, their intensities relative to peaks A and B increase if a 10% HI/He mixture is expanded through the pulsed molecular beam valve instead of the 10% HI/Ar mixture used in the results shown here. In addition, matrix isolation studies[21] on IHI^- have yielded a value of 129 cm^{-1} for the symmetric stretch frequency in the ion, in excellent agreement with the spacing between peaks A, a, and b. We therefore assign peaks a and b to hot band transitions originating from the $v_1"$ = 1 and $v_1"$ = 2 symmetric stretch levels of the ion and terminating in the same level of the neutral as peak A. The a/A intensity ratio yields a vibrational temperature of 100 K for the IHI^- ions.

Peaks A and B belong to a second progression. The peak spacing and widths agree with what the simulations predict for transitions to metastable [IHI] levels. The peaks are assigned to transitions between the $v_1"$ = 0 level of the ion and two different symmetric stretch levels of the [IHI] complex. This assignment is consistent with the noticeably different peak widths which imply that the transitions are to two distinct levels of the complex with different lifetimes. The widths yield lower bounds of 180 and 120 fs for the upper state lifetimes of A and B, respectively. Since the symmetric stretch vibration of

[IHI] is strongly coupled to the dissociation coordinate of the complex, it seems reasonable that the higher lying symmetric stretch level of the complex (peak B) should have a shorter lifetime. Similar trends have been observed in collinear scattering calculations on the Cl + HCl[48] and F + DBr[49] reactions. Note that a substantial portion of the width of peak A is due to the experimental resolution, so the upper state lifetime for this transition may be considerably longer.

The symmetric stretch levels of the [IHI] complex with v_3' = 4 lie 0.49 eV above the I + HI (v = 0) asymptote compared to 0.30 eV for the levels with v_3' = 2. The peak widths in Figures 3 and 4, however, indicate that the lifetimes of the v_3' = 4 levels are considerably longer, a striking and somewhat non-intuitive result. However, the v_3 antisymmetric stretch mode is poorly coupled to the dissociation coordinate of the [IHI] complex, so it is not necessary that incresed excitation in this mode should result in shorter lifetimes for the metastable states. In recent three-dimensional simulations of the IDI^- photoelectron spectrum, Schatz[50] found that transitions to [IDI] symmetric stretch levels with v_3' = 4 were indeed narrower than those to v_3' = 2. This effect clearly calls for further experimental and theoretical study.

We conclude this section by considering the threshold photodetachment spectrum for the transition to v_3' = 0 which is shown in Figure 5. The single broad peak in the photoelectron spectrum actually consists of a series of peaks spaced by an

interval that increases from 20 meV to 25 meV towards lower laser wavelength. This is quite distinct from the 12 meV interval seen in the other spectra. However, as discussed above, the simulations predict a qualitatively different interpretation for the $v_3' = 0$ feature in the IHI^- photoelectron spectrum. In contrast to the $v_3' = 2$ and 4 levels of [IHI], photodetachment to $v_3' = 0$ is expected to primarily access direct scattering I + HI wavefunctions rather than quasi-bound resonances. We must therefore search for another explanation for structure in the $v_3' = 0$ transition. Figure 5 shows that there is an approximate correspondence between the peak positions and the energetic thresholds for the asymptotic levels I + HI(v=0, j = 11-16). The thresholds for these asymptotic states are indicated in Figure 5. The thresholds in figure 5 are drawn assuming the threshold for I + HI (v=0, j=0) is at 3.79 eV, well within the error bars of the value of E^-_b for IHI^-, 3.80 ± 0.13 eV, used above. Our results therefore indicate that photodetachment to I + HI(v=0, j) is enhanced near the thresholds for formation of HI in high rotational states.

In his three-dimensional simulation of the IHI^- photoelectron spectrum, Schatz[25] also observed peaks in the transitions to $v_3' = 0$ levels of the complex which correspond to asymptotic I + HI rotational energy levels. However, his results show significant intensity down to the I + HI(j=0) level. The apparent drop in signal for $j < 11$ may indicate that on the real I + HI potential energy surface, the scattering wavefunctions

which asymptotically correlate to I + HI (v=0, j<11) do not have much amplitude in the region of the surface probed by photodetachment. This may indicate that low rotational states of HI(v=0) are relatively unreactive; if relatively few I + HI (v=0, j<11) collisions lead to reaction, then the corresponding scattering wavefunctions will not penetrate into the transition state region. Classical trajectory[51,52] and quantum scattering[53] calculations on the model Cl + HCl potential energy surface in Ref. 46 predict that rotational excitation of HCl(v=0) dramatically increases its reactivity. Our results are consistent with this type of effect occuring in I + HI.

In summary, the threshold photodetachment spectra of the v_3' = 2 and 4 peaks observed earlier in the IHI^- photoelectron spectrum show underlying structure which provides definitive experimental evidence for relatively long-lived metastable states of the [IHI] complex. The spectrum of the v_3' = 0 feature also reveals additional structure which may relate to the reactivity of HI rotational states. This interpretation of our results, if correct, means that even though a linear negative ion is photodetached, we can learn about the non-collinear dynamics of a chemical reaction. The comparison of the new higher resolution results with simulations of the photoelectron spectra is enlightening. On one hand, there are enough areas of agreement to be able to use the simulations in interpreting our data. On the other hand, the discrepancies should aid in constructing a more realistic potential energy surface for the I + HI reaction.

We plan to obtain threshold photoelectron spectra of IDI^- in the near future which should provide further insight into the interpretation of our results. In particular, we might expect that the peak spacing of progressions in the symmetric stretch of the [IDI] complex should be similar to the spacing seen in [IHI], whereas structure due to asymptotic I + DI rotational levels should be very sensitive to isotopic substitution.

c) $IDI^-(N_2O)$ Photoelectron Spectrum

An important direction for our photodetachment-based studies of the transition state is the investigation of cluster ions in which a bihalide anion is surrounded by a known number of solvating species, i.e. $IHI^-(S_n)$. There is no ambiguity concerning the number of solvating species since the ions are mass-selected prior to photodetachment. Photodetachment of the cluster ion generates a neutral collision complex surrounded by the solvating species; such an experiment may serve as a probe of condensed phase reaction dynamics. As a first step to studying larger clusters, we have obtained the photoelectron spectrum of $IDI^-(N_2O)$, shown in Figure 6. The spectrum was taken at 266 nm.

A comparison of the cluster ion spectrum with the IDI^- spectrum in Figure 2 indicates that the addition of an N_2O molecule has perturbed but not destroyed the structure seen in the spectrum of the bare ion. Both spectra show three peaks

assigned to even members of the v_3 progression in the neutral complex. The 0→0 transition is shifted toward lower electron energy by 0.100 eV in the cluster ion spectrum. Assuming that N_2O interacts much more strongly with IDI^- than with the [IDI] complex, then this shift yields the binding energy of N_2O with IDI^-. Another difference between the bare and clustered IDI^- spectra is that the spacing between the three peaks is slightly different. The $v_3' = 0$ and $v_3' = 2$ peaks are more widely spaced by 0.013 eV in the $IDI^-(N_2O)$ spectrum, and the $v_3' = 2$ and $v_3' = 4$ spacing is 0.007 eV *less* than in the bare ion spectrum.

The significance of these results may be best appreciated by considering the previous photoelectron spectroscopy work by Bowen and co-workers[54] on the series NO^-, $NO^-(N_2O)$, and $NO^-(N_2O)_2$. The structure of the NO^- photoelectron spectrum remains intact in the two cluster ion spectra but shifts towards lower electron kinetic energy by 0.22 eV in the $NO^-(N_2O)$ spectrum and by 0.48 eV in the $NO^-(N_2O)_2$ spectrum. These shifts were taken to be the binding energies of one and two N_2O molecules to NO^- and are of the same order as the shift seen in the $IDI^-(N_2O)$ spectrum. However, the small but significant changes in the peak spacing between IDI^- and $IDI^-(N_2O)$ were not observed in Bowen's results on the NO^- series. We believe this variation in the peak spacing results because, in constrast to the stable NO entity produced in Bowen's experiment, we form an unstable [IDI] complex which does not have a well-defined equilibirum geometry.

This leads to the following explanation for the different

peak spacings in the $IDI^-(N_2O)$ spectrum. In the cluster ion $IDI^-(N_2O)$, some charge transfer is expected from the IDI^- ion to the N_2O molecule. This can distort the IDI^- geometry, most likely by lengthening the interiodine distance since the extra electron is what holds the ion together in the first place. On the other hand, subsequent to photodetachment, it is a reasonable approximation to ignore the interaction between the [IDI] complex and neighboring N_2O molecule. Thus, the cluster ion photoelectron spectrum is, to first order, equivalent to the photoelectron spectrum of slightly distorted IDI^-.

Figure 7 shows a model collinear potential energy surface[42] for the I + DI reaction. The horizontal and vertical axes are proportional to the symmetric and antisymmetric stretch normal coordinates, respectively. The estimated equilibrium interiodine distance in IDI^- of R_e = 3.88 Å [23] corresponds to the solid vertical line drawn through the surface in Figure 7. A cut through the surface at this interiodine distance yields a double minimum potential which is, to a good approximation, the antisymmetric stretch potential for the [IDI] complex with an interiodine distance of 3.88 Å. This potential is shown in Figure 8 (solid line), along with the eigenvalues for the first few even v_3' levels. Suppose that the interiodine distance in $IDI^-(N_2O)$ is 0.05 Å greater than in the bare ion. The antisymmetric stretch potential for the [IDI] complex for this geometry is obtained by taking the cut through the surface

indicated by the dashed line in Figure 7. This potential and its first few even eigenvalues are shown in Figure 8 (dashed lines). The major difference between the two potentials is that the barrier between the two minima is higher at larger interiodine distance. While this pushes up all the eigenvalues, the $v_3' = 2$ level is the most strongly affected since it lies very close to the barrier. The result is that in the antisymmetric stretch potential associated with the cluster ion, the $v_3' = 0$ and $v_3' = 2$ levels are further apart, and the $v_3' = 2$ and $v_3' = 4$ levels are closer together. This is consistent with the experimentally observed peak spacings.

Thus, our simple picture qualitatively explains the experimental results. The photoelectron of a cluster ion such as $IDI^-(N_2O)$ allows one to probe different regions of the I + DI potential energy surface and also gives an indication of the nature of the interaction in the cluster ion. We plan to study the photoelectron spectra of similar cluster ions in the near future as a function of the type and number of solvating species.

SUMMARY

Negative ion photodetachment can provide a detailed probe of the transition state region of a chemical reaction. Examples are presented describing how one can study the I + HI potential energy surface by photodetaching the stable anion IHI^-. Results from two types of photodetachment experiments are presented:

photoelectron spectrscopy and threshold photodetachment spectroscopy. The latter, higher resolution technique shows considerably more structure and indicates the presence of relatively long-lived metastable states of the [IHI] complex. Results are also presented for the photoelectron spectrum of the cluster anion $IDI^-(N_2O)$ which probes a different part of the I + DI potential energy surface than the bare ion photoelectron spectrum.

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FIGURE CAPTIONS:

Figure 1. Photoelectron Spectrum of IHI^- at 266 nm. (ref. 32)

Figure 2. Photoelectron Spectrum of IDI^- at 266 nm. (ref. 29)

Figure 3. Threshold photodetachment spectrum of v_3 = 2 peak in IHI^- photoelectron spectrum. The points are spaced by 0.1 nm (approximately 10 cm^{-1}). (ref. 32)

Figure 4. Threshold photodetachment spectrum of v_3 = 4 peak in IHI^- photoelectron spectrum. The points are spaced by 0.1 nm. (ref. 32)

Figure 5. Threshold photodetachment spectrum of v_3 = 0 peak in IHI^- photoelectron spectrum. The points are spaced by 0.1 nm. The energetic thresholds for the asymptotic levels I + HI(v=0, j=11-16) are indicated, taking the threshold for I + HI(v=0, j=0) to be at 327.14 nm (3.79 eV). (ref. 32)

Figure 6. Photoelectron spectrum of $IDI^-(N_2O)$ at 266 nm. (ref. 29).

Figure 7. Model collinear potential energy surface for I + DI reaction proposed in ref. 42. The solid vertical line corresponds to estimated interiodine distance R_e = 3.88 Å in IDI^-. The dashed vertical line corresponds to estimated R_e = 3.93 Å in $IDI^-(N_2O)$. The modified hyperspherical coordinates ρ and z are (approximately) proportional to the symmetric and antisymmetric normal coordinates of the [IDI] complex. (ref. 29)

Figure 8. Antisymmetric stretch potentials and v_3 = 0, 2, and 4 energy levels for [IDI] complex obtained by cuts through I + DI potential energy surface in Figure 7 at interiodine distances of 3.88 Å (solid lines) and 3.93 Å (dashed lines). (ref. 29)

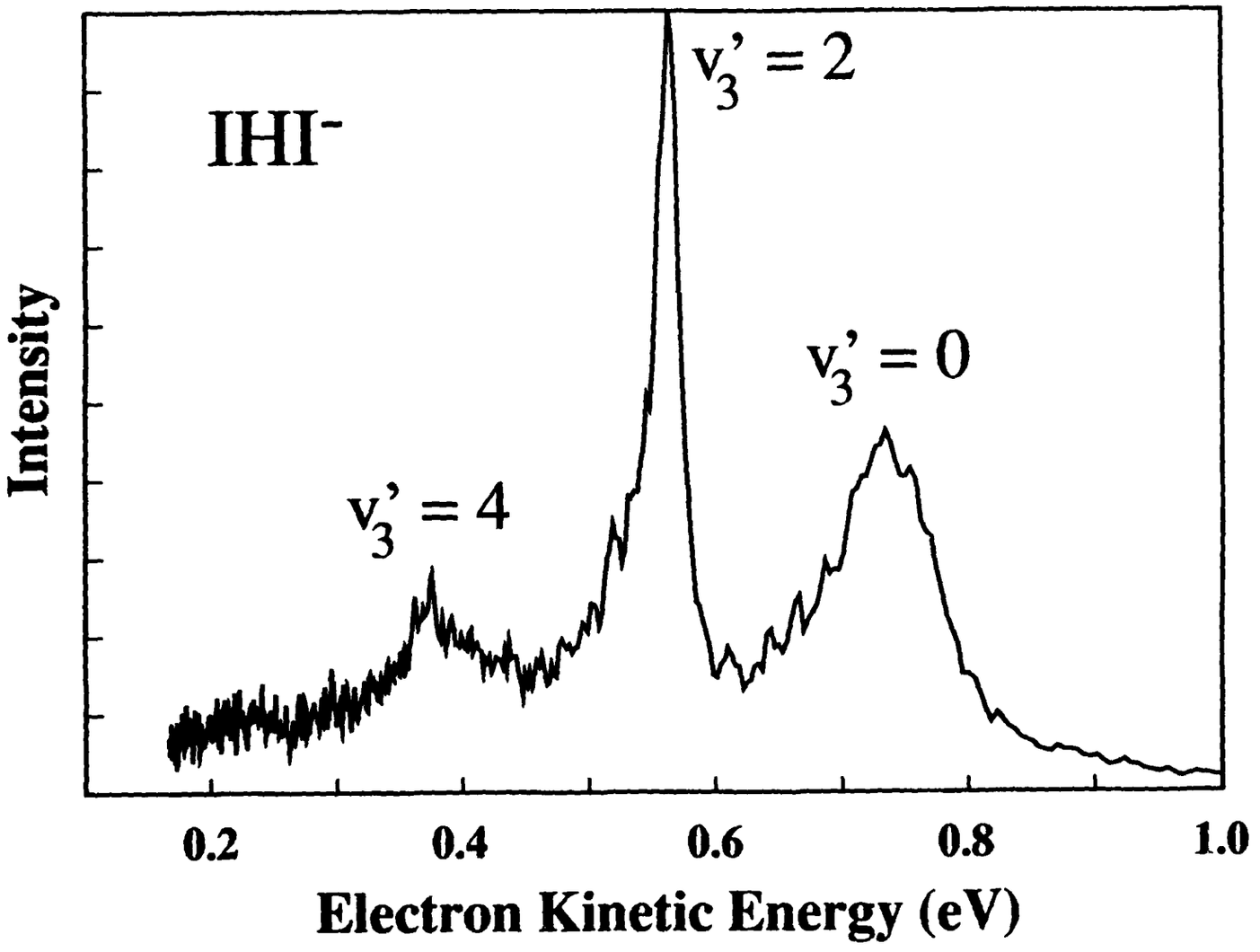
IHI⁻
$v_3' = 2$
$v_3' = 0$
$v_3' = 4$
Intensity
0.2
0.4
0.6
0.8
1.0
Electron Kinetic Energy (eV)

Fig. 1

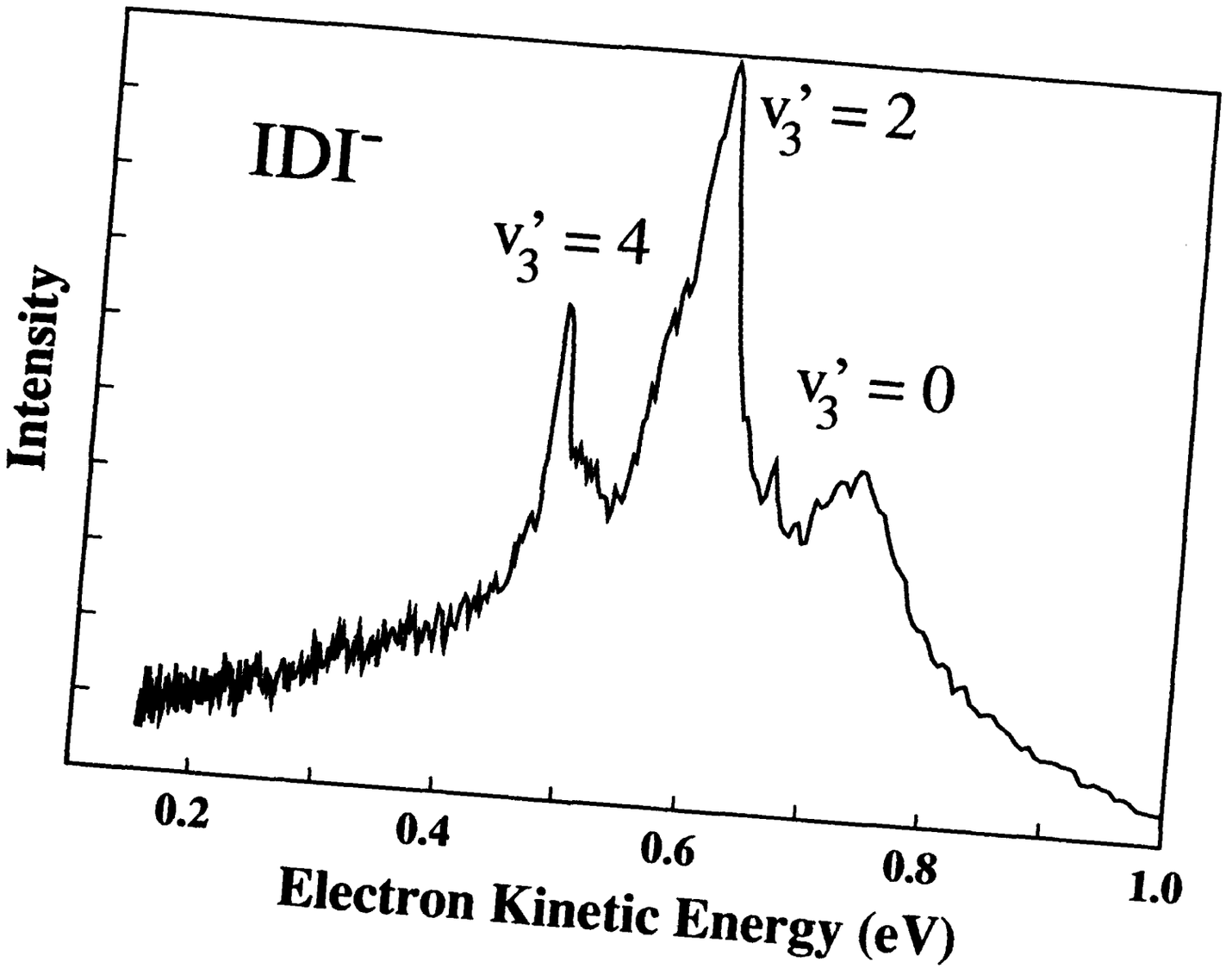
IDI⁻
$v_3' = 2$
$v_3' = 4$
$v_3' = 0$
Intensity
0.2
0.4
0.6
0.8
1.0
Electron Kinetic Energy (eV)

Fig. 2

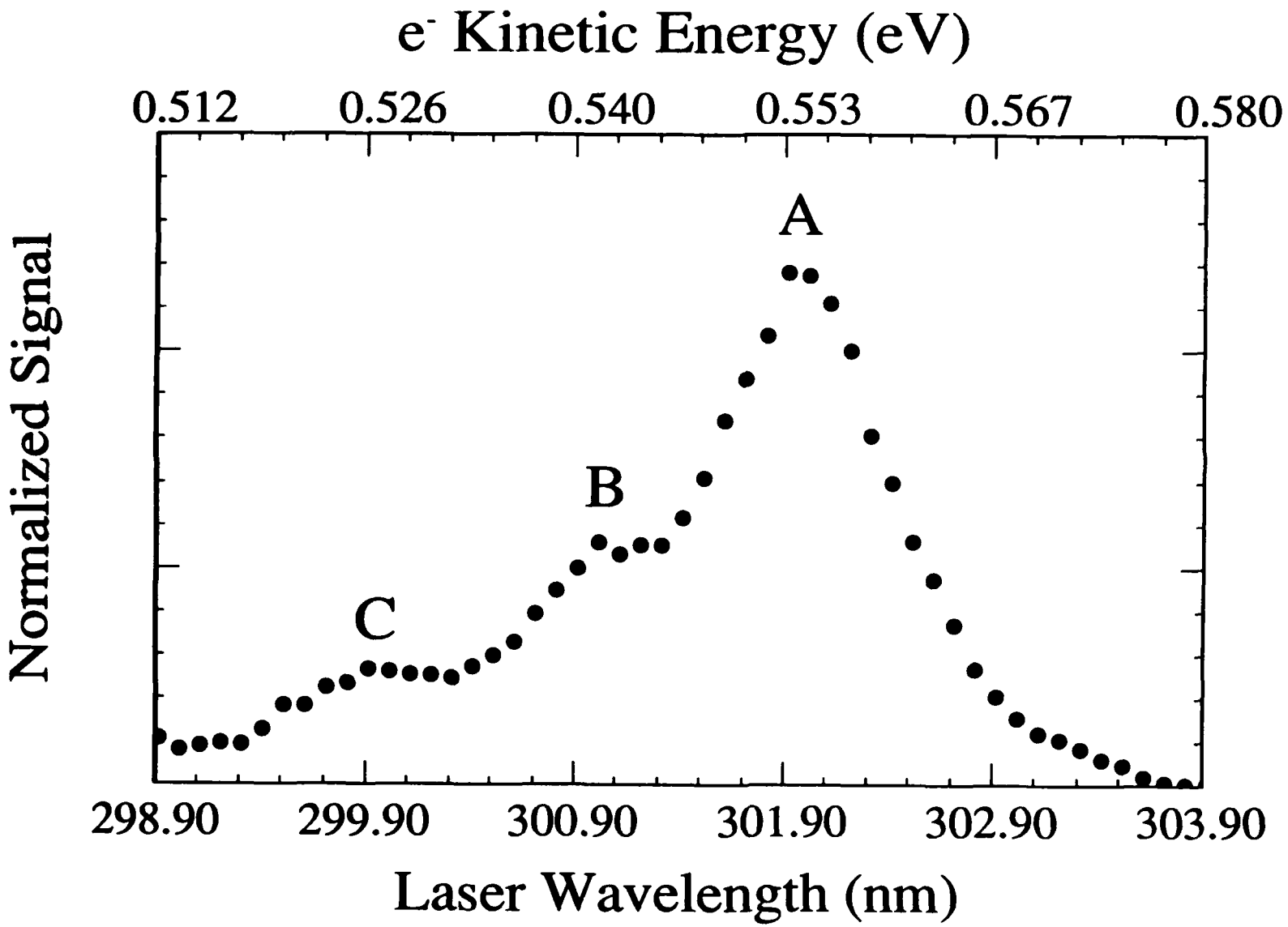
e- Kinetic Energy (eV)
0.512
0.526
0.540
0.553
0.567
0.580
A
B
C
Normalized Signal
298.90
299.90
300.90
301.90
302.90
303.90
Laser Wavelength (nm)

Fig. 3

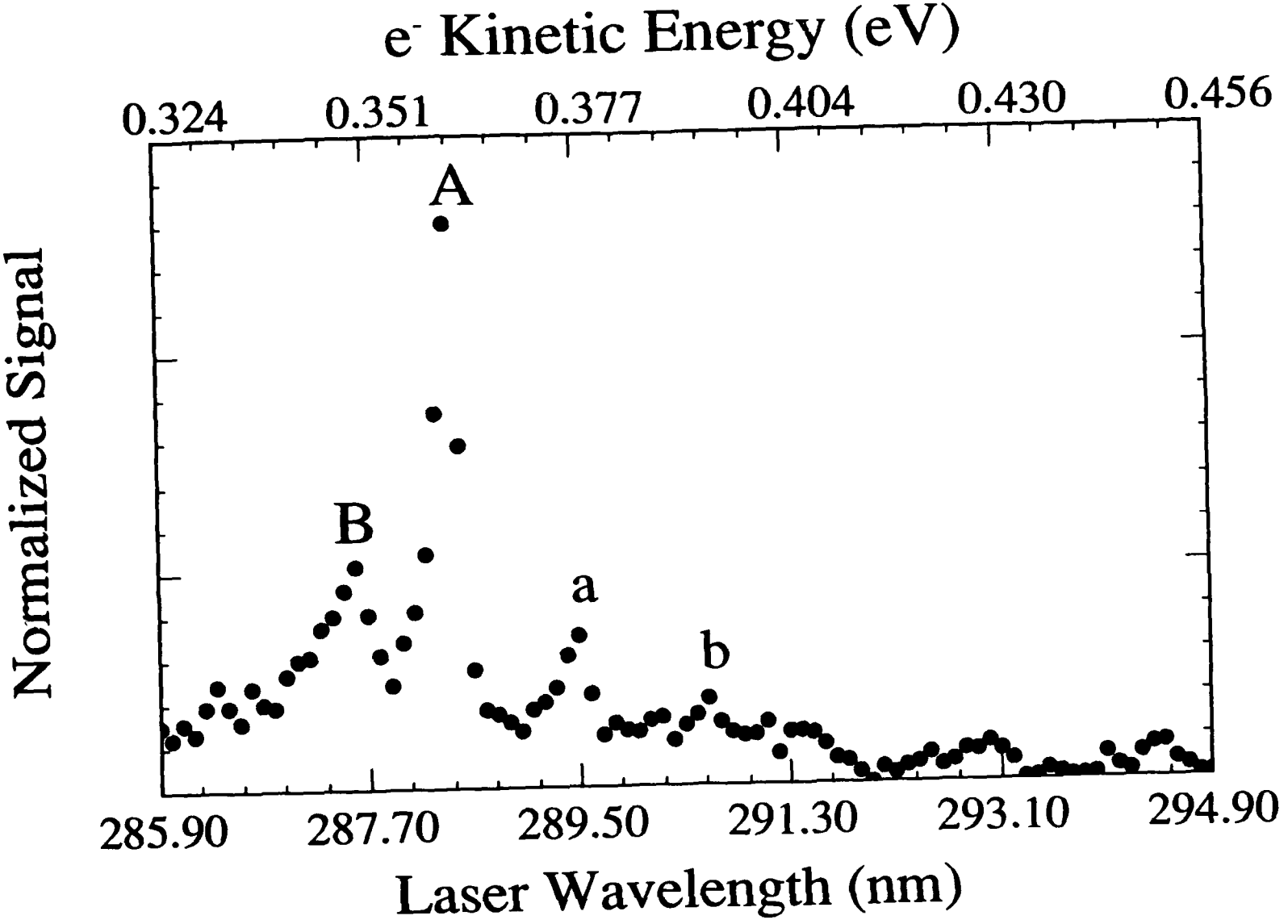
e⁻ Kinetic Energy (eV)
0.324
0.351
0.377
0.404
0.430
0.456
A
B
a
b
Normalized Signal
285.90
287.70
289.50
291.30
293.10
294.90
Laser Wavelength (nm)

Fig. 4

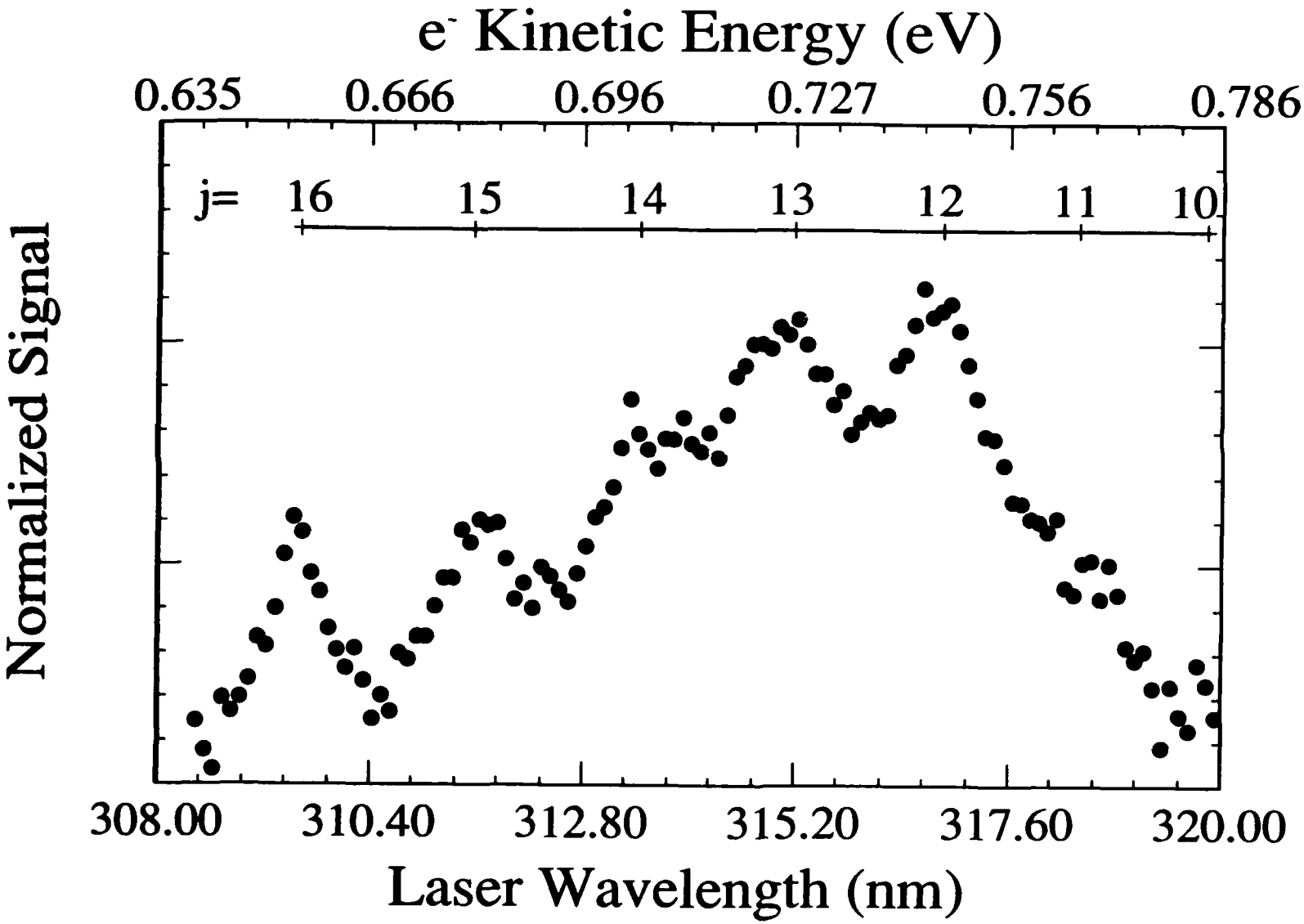
e⁻ Kinetic Energy (eV)
0.635
0.666
0.696
0.727
0.756
0.786
j=
16
15
14
13
12
11
10
Normalized Signal
308.00
310.40
312.80
315.20
317.60
320.00
Laser Wavelength (nm)

Fig. 5

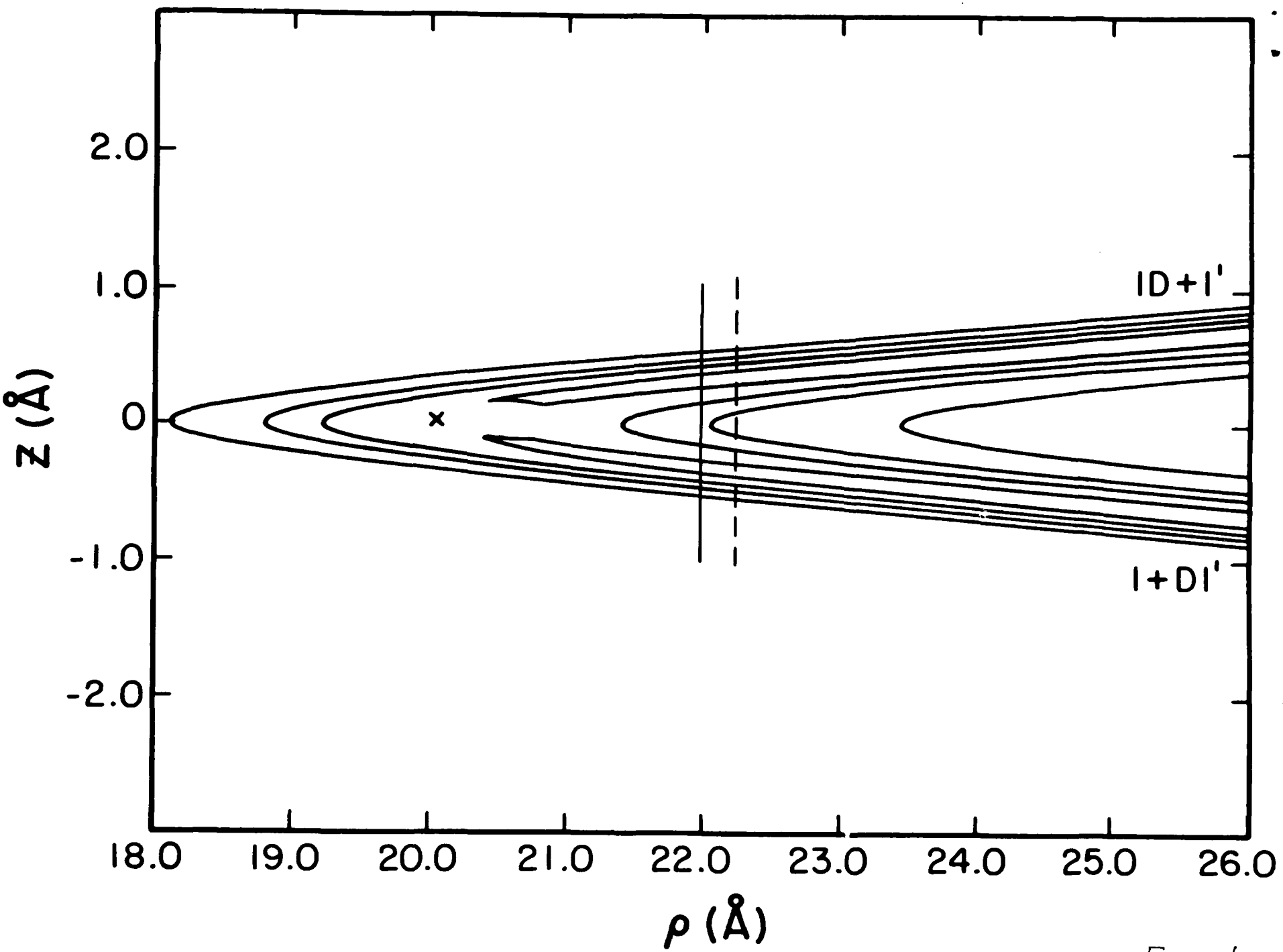

Fig. 6

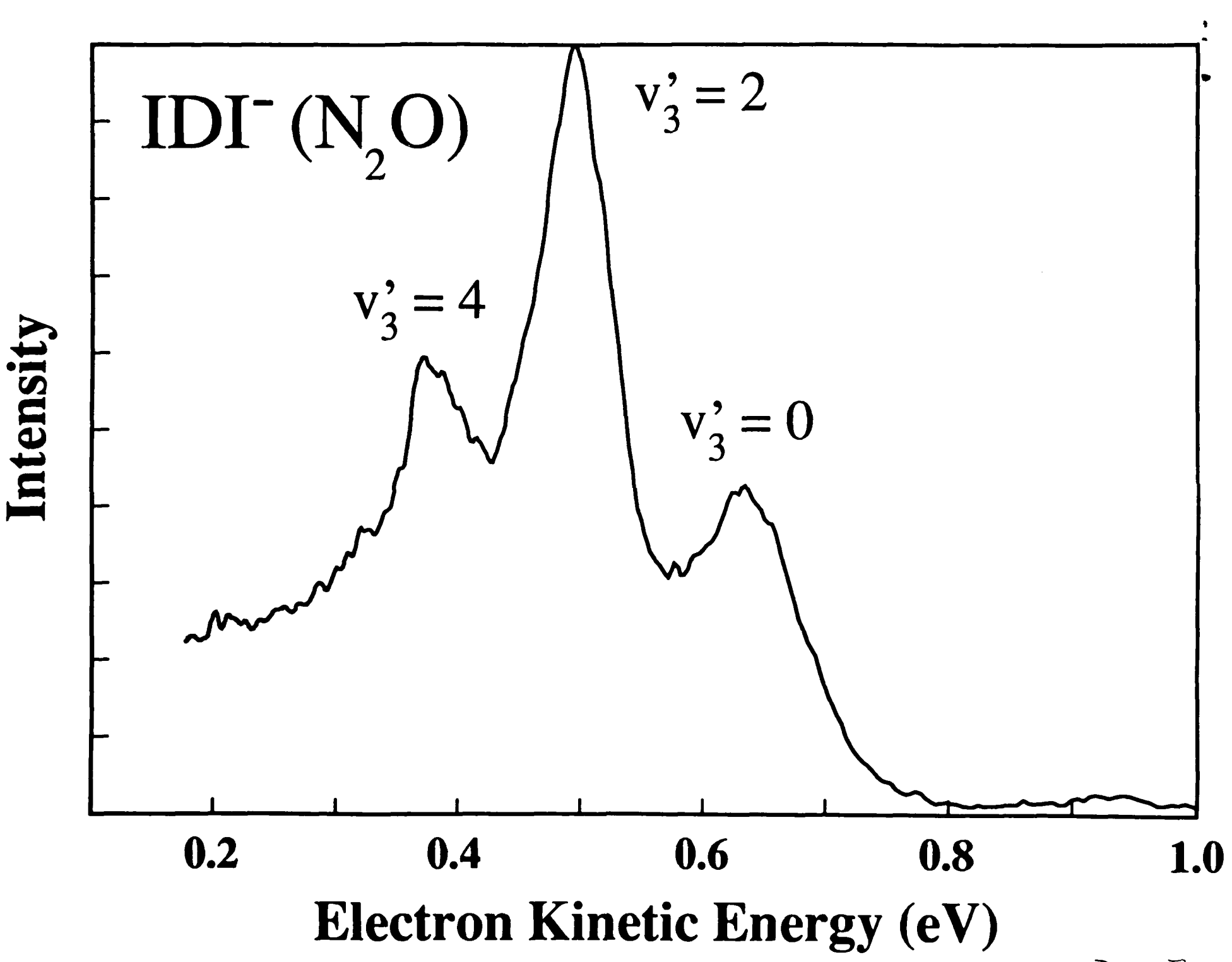
IDI⁻ (N2O)
v3' = 2
v3' = 4
v3' = 0
Intensity
0.2
0.4
0.6
0.8
1.0
Electron Kinetic Energy (eV)

Fig. 7

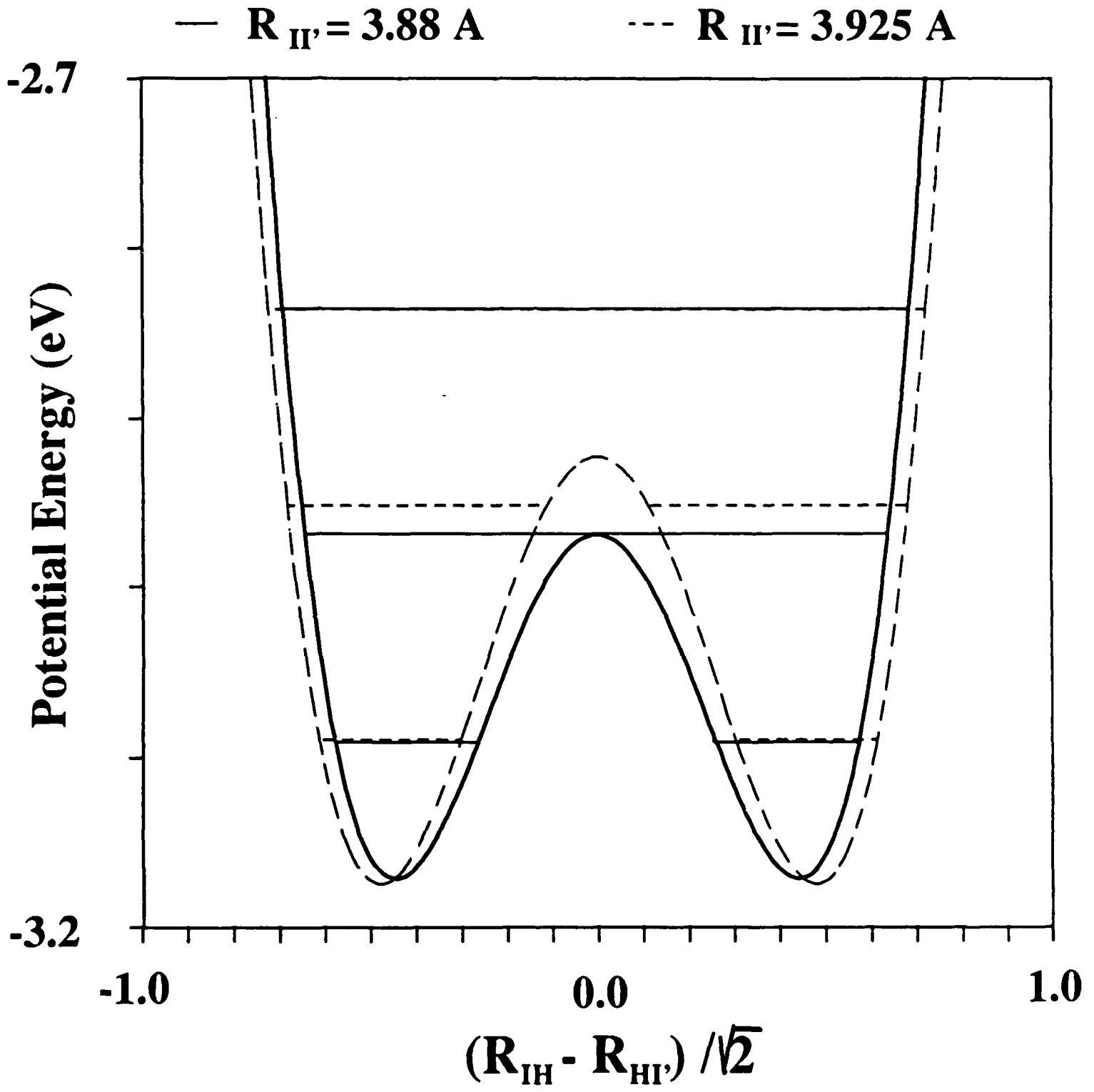

Fig. 8